Smart (6)

ON SOME POINTS OF INTEREST

CONNECTED WITH THE WANKLYN METHOD OF

SANITARY WATER ANALYSIS

PARTICULARLY ON THE DETECTION OF

RECENT SEWAGE

AND THE DETERMINATION OF THE

NATURE OF THE ORGANIC MATTER.

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NOT a great many years ago sanitary chemists affected a more precise knowledge of the organic matter in a water than those of the present day attempt to claim. Results were announced in grains per gallon; and the outside world conceived that the whole matter was understood. More recently the establishment of arbitrary scales of purity or impurity, based on the results of special processes, has taken the place of the former method of giving a verdict, and the outside world, when not trammelled by personal considerations, has acquiesced in this assumption of special knowledge. Occasionally, as a consequence of this, an analyst at the present time falls in the esteem of certain individuals when he acknowledges his inability to give full information concerning the organic matter in a water, to state positively whether a water is wholesome or unwholesome, or to detect a trace of sewage which is known, or strongly suspected, to be present. Even men well versed in the general principles of sanitary science, have, by these acknowledgments, been led to regard the laboratory work of the analyst as a kind of quasi-scientific hocus-pocus, which tells as little as the ancient oracle. The fact is that although the principles involved in these processes are incapable of indicating whether a specific morbific agency is present, they very frequently throw much light on the probable character of a water. Microscopical and biological inquiry will perhaps ultimately supercede the purely chemical methods; but the former are in their infancy as yet, and although very promising as children, it remains to be seen whether they will fulfill their promise. Meanwhile the work of the world in this line has to be performed by the chemical processes and it is encouraging to know that the more these are studied the more definite becomes the testimony they are capable of yielding.

I propose here to refer in particular to certain results of the Wanklyn process that are not generally appreciated. This process measures the free ammonia in a water and afterwards the albuminoid ammonia, or that formed by the breaking up of the nitrogenous organic matters. The former, when in relatively large quantity, and particularly in well waters, is usually due to cesspool, sewer, or privy connections. The latter is a measure of the existing impurity, and, if relatively large, is naturally suggestive of unwholesomeness. Wanklyn's arbitrary limits of wholesomeness are well known and need not be repeated.

It is generally understood or assumed that the results given by the same water are always identical. On the contrary they may be modified by the manner in which the process is conducted.

IMPERFECT CONDENSATION

of the evolved ammonia causes a loss which may vary from 1 to 12 per cent. of the total, according to the slowness or rapidity of the distillation

and the temperature of the current in the condenser. Slow distillation and a condensing current at winter temperatures give the minimum of loss; rapid distillation and a condensing current at summer temperatures, the maximum. This affects the total of both the free and the albuminoid ammonias; but the latter is affected even to a greater extent by the time occupied in the distillation, or by the

IMPERFECT CONCLUSION OF THE EXPERIMENT.

Wanklyn has acknowledged that his process is imperfect and that the whole of the nitrogen of the organic matter is not converted into ammonia; but he claims that, as the albuminoids in a water are of similar constitution, and yield up a definite percentage of their nitrogen, the results of the process in different instances are susceptible of comparison, and enable the operator to rate the water on an arbitrary scale. This claim is not wholly sustained by the results of recent investigations. The albuminoid ammonia does not pre-exist in the water; it is formed during the analytical operation, and requires time for its formation. The element of time is an important one. The nitrogen of some organic matters is slowly converted by boiling with the alkaline permanganate—so slowly that the experiment may reach its conclusion, by the disappearance of the water from the retort, before the whole of the nitrogen has been liberated as ammonia. This occurs with most of the alkaloidal substances. If an organic matter require boiling for two hours with alkaline permanganate to reduce and liberate its nitrogen a rapid progress of the experiment concluding the distillation in one hour will yield only a percentage of the nitrogen. A weak flame will give higher issues of albuminoid ammonia from the same organic matter than a strong flame, because it prolongs the action on the one hand, and lessens the loss from imperfect condensation on the other. In all instances in which the organic matter is slowly decomposed, the yield of albuminoid ammonia will vary with the time occupied by the distillation. Some waters will give very different results, according as the process is conducted at a rate of ten or of twenty minutes for each measure of 50 cubic centimeters distilled. It is needful to bear these irregularities and imperfections in mind, for some of them give important indications as to the source and quality of the organic matter.

DETECTION OF RECENT SEWAGE.

This may be effected by noting the peculiar behavior of urea when submitted to the Wanklyn process. A few nitrogenous substances are not decomposed by the action of the alkaline permanganate solution; among these Prof. Wanklyn includes urea. He is very positive on this point. He says: "Except in the instance of nitro-compounds, urea and ferrocyanide of potassium, we have not met with any unequivocal instance of failure of an organic nitrogenous compound to evolve ammonia in being heated to 100° C, with a strongly alkaline solution of permanganate." And again: "In presence of permanganate and excess of potash, urea is doubtless decomposed; but it yields no ammonia, which is a very extraordinary and noteworthy fact." And further: "On inquiring into the other peculiarities of structure which prevent alkaline permanganate evolving nitrogen of a given organic compound in the form of ammonia our attention is arrested by the example of urea which evolves none of its nitrogen as ammonia when so treated."

Nevertheless, urea yields about 22 per cent. of its nitrogen as ammonia when treated as Wanklyn treated the alkaloids and other organic substances in determining the amount of their nitrogen evolved as ammonia by permanganate; and if the conditions of the experiment be arranged to permit of a longer continuance of the action of the permanganate on the urea, the whole of its nitrogen will be accounted for, provided that due allowance be made for loss from imperfect condensation.

Urea in solution is resolved gradually into ammonia. This is hastened by boiling, and hastened yet more by boiling with alkaline permanganate. If a solution containing 1 mgrm. of urea in 500 c. c. of ammonia-free water be distilled, the first measure of 50 c. c. which comes over will contain a comparatively large quantity of ammonia, because during the time occupied by the liquid in reaching the point of ebulition a certain portion of the urea has been decomposed. The second measure will contain less, and the third, fourth and subsequent measures will each contain .01 mgrm. of ammonia, showing that boiling for the time ordinarily occupied in the distillation of 50 c. c. liberates the nitrogen necessary to form that amount of ammonia. Again, if a solution containing 1 mgrm. of urea and a charge of alkaline permanganate in 500 c. c. of ammonia-free water be distilled, the first measure of 50 c. c. which comes over will contain a relatively large quantity of ammonia. The second will contain less, and the third, fourth and succeeding measures will each contain .02 mgrm. of ammonia, showing that the presence of the alkaline permanganate has as strong an influence in effecting the decomposition of urea as is exercised by the boiling temperature. After all pre-formed ammonia has been liberated from an ureal solution an equable and persisting evolution takes place which may be represented by N in the absence of caustic alkali and permanganate, and by twice N in the presence of these reagents.

Dilutions of fresh or decomposing urine in tap water give similar results. When these are treated as water samples by the Wanklyn process there is first a liberation of the pre-formed ammonia, and afterwards an equable decomposition of the urea by the continued boiling. Then on the addition of the alkaline permanganate there is a comparatively free liberation of ammonia from the urea and other nitrogenous substances that may be present and afterward a persisting and equable evolution, each measure of 50 c. c. containing as much again as the corresponding measure distilled in the absence of the permanganate. This peculiarity in the behavior of urea is of importance, as by it the presence of this substance may be recognized in a water. It does not appear that any other substance gives issue to the free and the albuminoid ammonias in the manner stated. Many organic chemicals have been examined and also many organic substances, including the waste products of manufactures, etc., but not one was found to present reactions by which it could be comfounded with urea. Many gave a persisting and equable evolution of albuminoid ammonia, but few of these gave at the same time a persisting evolution of free ammonia; and where in some exceptional instances of factory drainings there was a persisting evolution of both free and albuminoid ammonia, these ammonias were not yielded in the proportion of 1:2.

Moreover the observations on the decomposition of urea have an approximatively quantitative value;—for since 1 mgrm. of urea in 500 c. c. of water gives a persisting and equable evolution of .01 mgrm. of ammonia when distilled alone or with sodium carbonate, as in the first half of the Wanklyn process, and

an evolution of .02 in each measure when subsequently treated with the alkaline permanganate, a water sample which yields such results must have contained urine equivalent to, at least, 1 mgrm. of urea. Thus, a water which yielded in successive distillates of 50 c. c., each .47, .25, .15 and .15 mgrm. of free ammonia, and afterward .54, .34, .32 and .32 mgrm. of albuminoid ammonia, respectively in each of four measures distilled from alkaline permanganate, might be set down as having contained urine equivalent to, at least, 15 mgrms. of urea in the 500 c. c. of water used in the experiment. The urea in urine is, of course, a variable quantity, but as the mean of a number of experiments on fresh urine, it was found that one half of a cubic centimeter in 500 c. c. of distilled water, or 1 part in 1000, yielded the returns given above as indicating the presence of 15 mgrm. of urea in the 500 c. c. treated by the Wanklyn operation. From these data the quantity of urine present in a given sample of polluted water may be approximately estimated.

The writer was so impressed with the importance and reliability of these observations on the persisting evolution of free and albuminoid ammonia from urea that on one occasion when an unknown water, sent to him for examination, yielded such results, he did not hesitate to report the water as polluted by so much urine per gallon. His purpose was to make this a test case; and he succeeded, although he was not informed of the fact until nearly two months afterward, when, having reported another unknown water as a rain water, shed from a clean roof and stored in a sound and clean cistern, he was made acquainted with the following particulars:—

Typhoid fever appeared in a cottage built by a gentleman as a summer residence. The quality of the water was suspected, and a sample analyzed by Prof. E. S. Wood was pronounced unfit for use. A second chemist having confirmed this verdict, a physician inspected the premises and suggested that sewer gases from the ventilating pipe of the water closets might have been condensed on the roof and washed thence into the cistern. Measures were taken to remedy this assumed evil, and the cistern was pumped out, cleaned and relined with cement. The water sample which was condemned as containing so much urine per gallon, was taken from this cistern after it had thus been subjected to careful and scientific treatment. Naturally, the proprietor was shocked; and, in view of his efforts to procure a fair rain water, felt disposed to question the analytical results rather than the quality of the water. Fortunately, however, Mr. E. W. Bowditch, of Boston, who was conducting the sanitary survey of the premises, conceived that further investigation was imperatively required. Ultimately in his examination he discovered that there were three apertures in the cistern, although only two conductors from the roof entered it. On inquiry it was remembered that a few years before, in making some additions to the cottage, a conductor had been disused, but what had been done with it was not known. The track of this old conductor was then uncovered at its cistern end, and followed to its termination in an open mouth a foot below the surface near the porch of the building. A luxuriant growth of vines rose from the surface at this point, and these vines were from time to time nourished with chamber slops. It was moreover found to be the custom of the house to collect all such slops in pails which were emptied through a water closet on the first floor and then set out on the roof of the piazza to air. The old conductor was removed and its cistern aperture sealed, and the connection was cut between the cistern and the roof of the piazza. When the water again accumu-

lated after these changes had been effected, the sample submitted for analysis was reported as a satisfactory rain water. This appears to illustrate the value attaching to the manner in which the ammonias come over during the distillations of the Wanklyn process, and it is specially mentioned here on account of the difficulty encountered in verifying the accuracy of the chemical results. Many other illustrations might be given, but they are unnecessary.

ANIMAL OR VEGETABLE MATTER.

Wanklyn has observed that when a water containing vegetable matter is distilled with the alkaline permanganate solution the albuminoid ammonia comes over very slowly. In verifying the accuracy of this statement, it was found that the rapidity of the evolution was determined by the instability of the matter, or its tendency to a state of putrescence rather than by its derivation. Pure animal and pure vegetable albuminoids gave up their nitrogen as ammonia at an equal pace when equal times were occupied in the distillation of the various measures. Thus, if the first measure of the distillate contained .24 mgrm., the second would contain .12, the third .06, the fourth .03, etc. But if these matters were in a decomposing condition, the second, third, and subsequent measures would each contain only one-third of the ammonia found in the measure that immediately preceded it. Animal matters, however, more readily pass into the putrefactive condition, so that when the organic matter of a water gives up its nitrogen after the manner first stated, there is a strong probability of its derivation from the vegetable kingdom; and this probability is rendered almost a certainty if a comparatively large quantity of oxygen is required for its oxidation when treated by the Kubel or Tidy method.

But vegetable matter in a state of fermentative change reveals itself during the Wanklyn process in two ways, neither of which appears to have been appreciated by any of the many analysts who make use of this method of sanitary analysis. The color produced by the Nessler reagent in a weak ammoniacal solution varies from a pale straw color to a dark sherry brown; but occasionally in testing the distillates of the Wanklyn process, particularly those containing the free ammonia, a green coloration masks the brown of the ammonia and prevents the accurate estimation of the volatile alkali. If there be but a trace of ammonia present, the color may be an olive-green, or even a citron-green, with generally a tendency to the development of a haziness in the liquid. No explanation of this color-interference has been furnished, although some years ago a reference was made to it at a meeting of the English Society of Public Analysts. Wanklyn does not even mention its occurrence.

The frequency with which this color-interference was encountered in certain experiments on water washings of air drawn over fermenting vegetable refuse, led me to conceive that it was due to an ethylic compound formed during the fermentation. A reference to my laboratory note books speedily showed that the green color was always associated with waters known to contain decomposing vegetable matter. In one instance the bilge-water of a sugar ship from Cardenas, Cuba, had given such an evolution of this coloring agent that Wanklyn's process was wholly inapplicable as an analytical method on account of the impossibility of effecting color comparisons. Experiments with ethylic ether and alcohol, with cane sugar, starch, glucose, tannin, and fermenting vegetable matter always developed the greenish coloration and haziness. More-

over, it was noticed that watery dilutions of these substances invariably struck a deep yellow color with sodium carbonate; and another reference to former laboratory work disclosed the fact that in all cases characterized by the green coloration of the Nesslerized distillate, the water had developed a yellow color on the addition of sodium carbonate for the liberation of the free ammonia. The yellow color thus assumed and the green coloration subsequently interfering with the Nessler reaction were therefore regarded as indicating the presence of non-nitrogenous vegetable substances in the progress of fermentative change. Hence, to summarize:

A water yielding up the nitrogen of its organic constituents slowly as albuminoid ammonia contains *recent organic matter*,—

Of *animal* derivation, if a small quantity of oxygen be required to oxidize it by the Kubel or Tidy process,—

Of *vegetable* derivation, if a large quantity of oxygen be required.

A water yielding up the nitrogen of its organic constituents more rapidly contains *decomposing organic matter*,—

Of *animal* derivation, if a small quantity of oxygen be required to oxidize it, and if there be no interference with the development of the true ammonia coloration during Nesslerization,—

Of *vegetable* derivation, if a large quantity of oxygen be required, and if a yellow coloration be developed in the water on the addition of sodium carbonate and a greenish color interfere with the estimation, particularly of the free ammonia, by Nessler's method.